SURVEY REPORT

MOBILE TAGA SURVEY
SUNOHIO MOBILE PCB
DESTRUCTION FACILITY
FIRESTONE STEEL PRODUCTS, LONDON
DECEMBER, 1986

ARB-052-87

MAY 1987

Ontario
Ministry of the Environment

E. PICHÉ, Director
Air Resources Branch

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- prepared for -

The Southwestern Region
Ontario Ministry of the Environment

- prepared by -

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Executive Summary

On December 9 and 10, 1986, the mobile TAGA unit conducted an air monitoring survey at the Firestone Steel Products Plant in London, Ontario. The survey objective was to provide near real-time measurements of ambient PCBs during the decontamination of three active electrical transformers containing up to 1400 ppm of PCBs. The transformers were decontaminated by Sunohio Canada Incorporated using a mobile PCB destruction unit.

During the 2 day survey period, a total of 225 2-minute air samples were screened for selected PCBs using the Ministry's mobile TAGA unit. None of the 15 1/2-hour averaged concentrations of PCBs exceeded the Ministry guideline of 0.45 $\mu g/m^3$. In fact, all readings for ambient PCBs were below the analytical detection limits (0.07$\mu g/m^3$), despite sampling just 0.5 metres from Sunohio's exhaust vent.

1.0 INTRODUCTION

As requested by the London District Office of the Southwestern Region, the mobile TAGA (Trace Atmospheric Gas Analyzer) unit of the Air Resources Branch conducted an air monitoring survey in London during the week of December 8, 1986. The purpose of the survey was to provide, on-site, ambient concentrations of selected PCBs in the vicinity of Sunohio's mobile PCB destruction facility. Sunohio Canada Incorporated had been contracted to decontaminate PCB tainted mineral oil from three transformers located at the Firestone Steel Products Plant in London.

This exercise was of historical significance for it was the first time a mobile PCB destruction facility was permitted to operate commercially in Ontario. The technology used by Sunohio is based on the reaction of molten sodium with chlorinated biphenyls. What makes the Sunohio process somewhat unique is that it is continuous; contaminated oil is withdrawn from an active transformer, treated and returned to the same transformer.

In accordance with the Provincial Certificate of Approval, the Sunohio facility would have been shut down had the PCB monitoring results shown ambient concentrations in exceedance of 450 ng/m^3 for a thirty minute averaged concentration. The operation would not have been permitted to continue until the reason for the possible excess emissions had been determined and the problem corrected.

The mobile TAGA unit provided PCB analysis of ambient air samples during several hours of Sunohio's operation on December 9 and 10, 1986. Throughout the survey the TAGA scientists relayed the monitoring results to Mr. C. Murray of the Ministry's London Regional Office. This report summarizes both the analytical protocol and the findings obtained by the mobile TAGA unit during the destruction of the PCBs by Sunohio.

2.0 TAGA TECHNOLOGY AND SURVEY STRATEGY

A detailed description of the PCB monitoring technique is provided in Appendix A. Briefly, the TAGA (model 3000) is a specialized quadrupole mass spectrometer mounted in a 26-foot GMC transmode. Owing to the TAGA's unique atmospheric-pressure chemical ionization source and vacuum system, air may be sampled directly, allowing for the rapid analysis of pollutants on-site. When monitoring for PCBs the ion source is coupled to an Automated Short Term Adsorber (ASTA), which is simply a device designed to preconcentrate the ambient PCBs. The TAGA/ASTA technique provides ambient PCB measurements in 2-minute intervals, with a 1/2-hour averaged concentration being the result of 15 consecutive 2-minute samples. In this study the air was screened for the di, tri, tetra and pentachlorobiphenyl congeners.

Essentially the survey strategy for the mobile TAGA was to position the unit downwind of the alleged source. The ambient PCB levels were then determined every 2 minutes and compared to previously completed background, or upwind, data. However, on the second day of this survey the strategy was modified to compensate for inaccessibility. To ensure that samples were extracted from points downwind of the main emission point, a sampling funnel was placed on the roof of the PCB destruction unit approximately 0.5 metres downwind of the oil furnace vent. Six metres of plastic sampling hose (4 cm inner diameter) connected the funnel directly to the TAGA inlet.

Prior to the start of the PCB destruction process, the TAGA was calibrated for PCBs and several hours of background data were acquired. The background data were used to correct the downwind measurements. Calibrations were also performed at least twice daily on days when Sunohio was operative. Detection limits for total PCBs monitored were 0.05 $\mu g/m^3$ on December 9, and 0.07 $\mu g/m^3$ on December 10, 1986. The relative standard deviations were better than 5% for multiple injections of PCBs at the 0.425 $\mu g/m^3$ level.

3.0 RESULTS AND DISCUSSION

On December 9, 1986, the mobile TAGA unit arrived at Firestone and commenced with the pre-survey screening of the site for airborne PCBs. It was confirmed that there were no local sources which might have contributed significant amounts of chemical interferences to the PCB target masses at either the location of the PCB destruction unit or the location of the TAGA. Background monitoring conducted prior to the start-up of the PCB destruction facility indicated non-detectable levels of volatile PCBs. As an added precaution against potential chemical interferences, Firestone provided both the TAGA and Sunohio trailers with hydro so as to eliminate the need to operate generators.

At 16:30 hours the TAGA was moved to a location beside the Sunohio trailer and began downwind monitoring. Our sampling point, which is situated one metre above the roof of the unit, was approximately six metres from Sunohio's main point of emission, the oil furnace exhaust vent.

Sunohio began destroying PCBs from the first of three transformers shortly after 18:00 hours. As seen in Table 1, between 16:25 and 21:12 hours seven (7) 1/2-hour averages indicated that there were no PCBs present. In fact, PCBs were not detected above the detection limit of 0.05 $\mu g/m^3$ in any of the 105 individual 2-minute air samples. (Recall that a 1/2-hour averaged concentration consists of 15 2-minute air samples.) At the time of sampling the winds were very light and the ambient temperature was 6°C. The response factors utilized to quantify PCB levels were confirmed at 19:23 hours by spiking the ambient air samples with 0.425 $\mu g/m^3$ of the PCB standard.

The PCB monitoring by the TAGA crew was halted at 21:15 hours, and recommenced the following morning. Apparently, Sunohio was not handling PCBs between 22:30 hours and 8:30 hours of the next day.

In the morning of December 10, the ambient temperature had fallen to -6°C and the winds were of moderate strength from the west. Consequently our monitoring location was no longer downwind and relocation to the east side of the Sunohio facility was impossible. As alluded to previously, a funnel connected by a hose was placed downwind of the Sunohio trailer to ensure downwind monitoring.

Commencing at 10:30 hours, 120 2-minute samples were analysed for selected PCBs by the TAGA unit. As observed the previous evening, no PCBs were detected above the analytical detection limit (0.07 $\mu g/m^3$). The Ministry guideline for PCBs of 0.45 $\mu g/m^3$ was not exceeded by any of the 8 1/2-hour averaged concentrations.

Again the PCB response factors were verified at 16:18 hours by spiking the air samples with known amounts of PCBs. A decrease in sensitivity of only 15% was observed over the 6 hour monitoring period. The survey was concluded at 16:45 hours on December 10, after none of the 225 2-minute air samples exhibited any PCBs above the analytical detection limits.

Table 1: TAGA PCB Survey - Sunohio Mobile PCB Destruction Facility
Firestone, London

SAMPLE #	DATE	START[1] TIME	1/2-Hr. CONC.[2] ($\mu g/m^3$)	COMMENTS
1-1	9/12/86	16:25	ND[3]	Prior to start - Background, no wind, light rain
1-2	9/12/86	16:56	ND	Prior to start - Background, no wind, light rain
1-3	9/12/86	18:13	ND	PCBs destroyed, beside trailer, no wind
1-4	9/12/86	18:45	ND	PCBs destroyed, beside trailer, light wind
1-5	9/12/86	19:38	ND	PCBs destroyed, beside trailer, light wind
1-6	9/12/86	20:10	ND	PCBs destroyed, beside trailer, light wind
1-7	9/12/86	20:42	ND	PCBs destroyed, beside trailer, light wind

Note 1: Start time refers to the start of each 1/2-hour average.
2: 1/2-hour conc. = average of 15, 2-minute samples; sum of the di to pentachlorobiphenyls.
3: ND = not detected above the detection limit of 0.05 $\mu g/m^3$ for total PCBs.
4: Meteorological data not recorded due to close proximity of buildings.

Table 2: TAGA PCB Survey - Sunohio Mobile PCB Destruction Facility Firestone, London

SAMPLE #	DATE	START[1] TIME	1/2-Hr. CONC.[2] ($\mu g/m^3$)	COMMENTS
2-1	10/12/86	10:31	ND[3]	PCBs destroyed, downwind (sampling vent), steady west wind
2-2	10/12/86	11:03	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-3	10/12/86	12:37	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-4	10/12/86	13:18	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-5	10/12/86	13:50	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-6	10/12/86	14:30	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-7	10/12/86	15:02	ND	PCBs destroyed, downwind (sampling vent), steady west wind
2-8	10/12/86	15:33	ND	PCBs destroyed, downwind (sampling vent), steady west wind

Note 1: Start time refers to the start of each 1/2-hour average.
2: 1/2-hour conc. = average of 15, 2-minute samples; sum of the di to pentachlorobiphenyls.
3: ND = not detected above the detection limit of 0.07 $\mu g/m^3$ for total PCBs.
4: Exhaust vent sampled "directly", see text.

APPENDIX A

Air Resources Branch

Continuous PCB Monitoring Technique

Mobile TAGA/ASTA

London - December (1986)

RE147

TAGA TECHNOLOGY

In 1979 the Air Resources Branch of the Ontario Ministry of the Environment acquired a mobile Trace Atmospheric Gas Analyzer (TAGA) from Sciex Incorporated of Thornhill, Ontario. The mobile TAGA unit (MAMU No.3) has been applied to a variety of air monitoring situations, including airborne PCBs. The Ministry has conducted over 50 air quality surveys with the mobile TAGA unit.

The TAGA 3000 is simply a specialized quadrupole mass spectrometer coupled to a unique sampling inlet and ion source (See Figure A1). Ionization of pollutants is achieved through chemical ionization, initiated by a stable corona discharge operating at atmospheric pressure. Since the ion source permits continuous, direct, air sampling at a high flow rate (100 l/min), it is possible to determine the temporal and spatial distribution of selected pollutant levels. The mobile TAGA's capabilities are especially suitable for plume tracking; that is, tracing a pollutant back to its source of origin.

When equipped with the standard atmospheric-pressure chemical ionization (APCI) source the TAGA system is sensitive to most volatile compounds containing a heteroatom, such as N, O, S, P and halide. Typical detection limits are in the range of 0.1 to 10 ug/m^3 depending on the type of chemical measured and the sample matrix.

The mobile TAGA unit is also equipped with a 10 metre, telescopic tower and meteorological instrumentation to measure local wind speed, wind direction and ambient temperature. All meteorological data are stored by the on-board computer simultaneously with the collection of air quality data. The data are instantly displayed on the CRT unit allowing the operator to assess the data on-site and thus formulate the appropriate survey strategy.

PCB MONITORING METHODOLOGY

For most chemical classes the sensitivity of the TAGA is extraordinary for ambient air monitoring. However PCBs are an exception, because the absolute sensitivity is insufficient for instantaneous real-time detection. Thus in the late 1970s Sciex Inc. developed a simple sampling device to preconcentrate volatile PCBs. Preconcentrating the PCBs for only 2-minutes lowers the detection limit by two orders of magnitude.

ASTA

Although the basic principles have remained unchanged, today's PCB preconcentrator has evolved into a portable sampling inlet system with all operating parameters under strict computer control. It is commercially known as the Automated Short Term Adsorber or ASTA.

The ASTA, shown in Figure A2, consists of two sample probes formed by coiling a nichrome wire, coated with a gas chromatographic stationary phase, OV-17. The positions, and thus functions of the two probes, are interchangeable between the adsorption or sampling position, and the desorption or analysis position. While one probe is adsorbing PCBs from the ambient air, the other probe is being desorbed and analysed for PCBs from a previous air sample. Altering the positions of the two probes permits continuous screening of the ambient air in 2 minute intervals. There is approximately an eight second delay between sampling periods due to the probe cycling time. Thus a "½-hour sample", which consists of 15 consecutive 2 minute samples, takes 32 minutes.

Sampling

When sampling for PCBs the probe is placed directly in the ambient gas stream (1.7 l/s) for a period of 2 minutes. The probe is then changed to the desorb position and 12 volts DC (3.25 amperes) are applied to the probe for a period of 40 seconds. This causes the probe

temperature to rapidly increase to approximately 300°C, thereby transferring the PCBs from the OV-17 into the gas phase. The carrier gas, which is a mixture of ultra pure zero air and benzene (100 ppm), constantly sweeps the PCBs into the ion source. Upon entering the ion source the PCBs immediately undergo benzene chemical ionization, producing molecular PCB ions (M^+) which are (mass) selectively monitored by the quadrupole mass filter.

The software allows for the screening of 4 PCB congeners at 8 masses, 2 isotopes per congener. Normally the dichlorobiphenyl to pentachlorobiphenyl species are monitored. There are two reasons for this: firstly, the TAGA is more sensitive to these species, and secondly, PCBs with lower molecular weights generally exhibit higher vapour pressures, thus increasing the likelihood of gas phase detection.

Calibration

Calibration of the system, including sampling probe adsorption efficiencies and TAGA response, is accomplished by continuously injecting known amounts of PCBs directly into the air sampling stream via a heated injection port (300°C) using a gas-tight syringe and motorized syringe drive. The PCB standards are prepared by the dissolution of pure PCB isomers, one per congener, into iso-octane. Repeated injections at 5 different syringe drive settings establishes a calibration curve which is linear (correlation coefficients are usually better than 0.995) over the PCB concentration range of 0.425 to 2.5 ug/m^3 per congener (See Figure A3). The relative standard deviations for multiple injections of PCB standards are typically better than 5% at the 0.425 ug/m^3 level.

DATA PROCESSING AND INTERPRETATION

Immediately following a desorption of the probe, the TAGA computer calculates the level of PCBs (or equivalents) per congener, per isotope, from the net signal (sample minus background) and the daily calibration factors. In fact, for each PCB congener group, two measurements are made: one for the chlorine 35 isotope (M), and one for the corresponding chlorine 37 isotope (M+2).

Criteria

At this stage the field survey scientist interprets the reduced data using the following criteria:

1) the adsorption peak (integrated signal) must be at least 3 times greater than the probe noise (S/N>3);

2) the PCB levels for a given isotope pair must be within the overall experimental accuracy of 20%;

3) the calculated isotope ratios must be within 10% of the theoretical isotope ratio for a given congener.

If condition 1) above is not satisfied, the congener concentration will be considered below the detection limit and a ND is reported. If conditions 2) and 3) are not evident then a chemical interference at one, or both, of the congener masses is assumed to be present, and the lower concentration value of the two isotopes is assigned the upper concentration limit for that particular PCB congener. The value is then flagged with the letter "i" indicating that a chemical interference has inflated the reported concentration. An example of a data print-out showing the PCB desorption curves may be seen in Figure A4.

Detection Limit

The PCB detection limit for the TAGA/ASTA technique is defined as being 3 times the standard deviation of the background signal observed

at the PCB masses, divided by the appropriate calibration factors. Thus by definition, the detection limit depends on two important factors:

i) the sensitivity, which is a function of the probe adsorption efficiencies and the benzene chemical ionization rates.

ii) the level of the interferences (adsorbed compounds that have the same nominal ionic mass as the targeted PCBs in both upwind and downwind air samples). Interference levels are highly variable depending on the sampling site, the source(s) in the immediate area, and the local meteorological conditions.

During a survey air samples are spiked periodically with 0.425 ug/m^3 per PCB congener to establish the daily sensitivity factors and determine, on-site, the detection limits of the technique. Typical detection limits range from 0.01 to 0.05 ug/m^3 per congener, or from 0.04 to 0.20 ug/m^3 for total (di to pentachlorobiphenyls) PCBs, depending on the complexity of the sample matrix.

SUMMARY

The TAGA/ASTA PCB monitoring technique is a specialized application of the mobile TAGA 3000. It was developed to rapidly screen the ambient air for volatile PCBs. Important features of the technique to consider when assessing the data are:

1) The technique was developed to measure gas phase PCBs. (Should non-volatile PCBs be trapped by the probe they would be reported as volatile PCBs and included in the total amounts.)

2) PCB levels are determined continuously every 2 minutes.

3) Four congeners are monitored simultaneously (normally the dichlorobiphenyls to pentachlorobiphenyls).

4) The detection limits for total PCBs typically range from 0.04 to 0.20 ug/m^3 depending on the sample matrix.

In summation, the mobile TAGA/ASTA technique is a rapid screening method for volatile PCBs, providing near real-time detection at the time when PCBs are potentially released into the atmosphere. It is the only method currently available to the Ministry by which the ambient air can be instantaneously scanned for PCBs, providing valuable information, on-site, necessary for assessing the environmental impact of the PCB destruction process.

RE049

TAGA 3000 SYSTEM

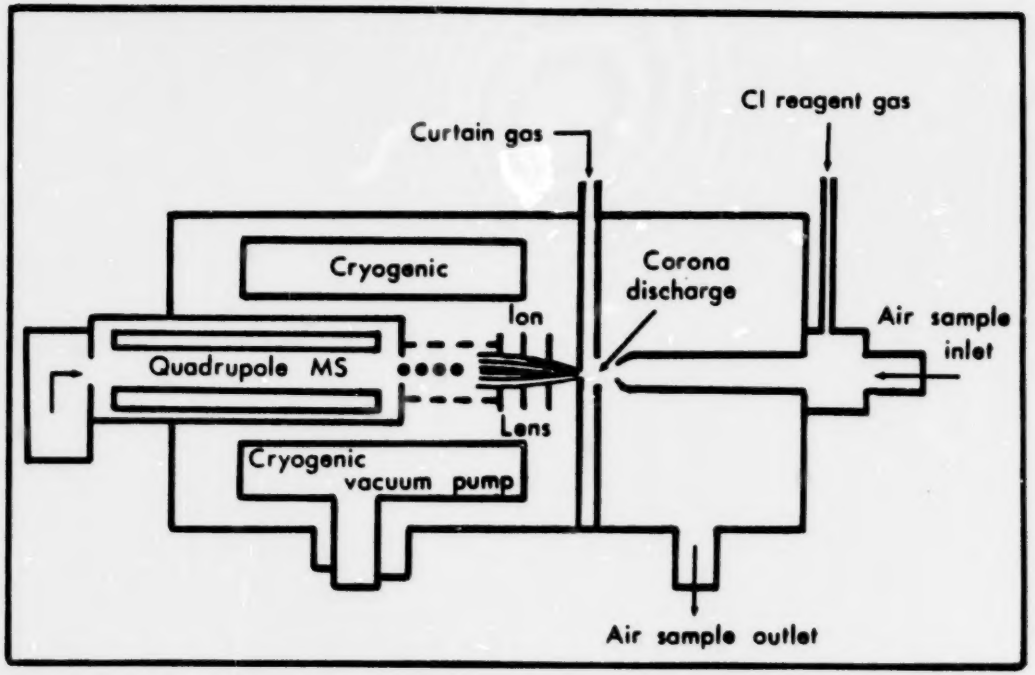


FIGURE A1: SCHEMATIC OF THE TAGA 3000 SYSTEM INSTALLED IN MAMU #3

ASTA SCHEMATIC

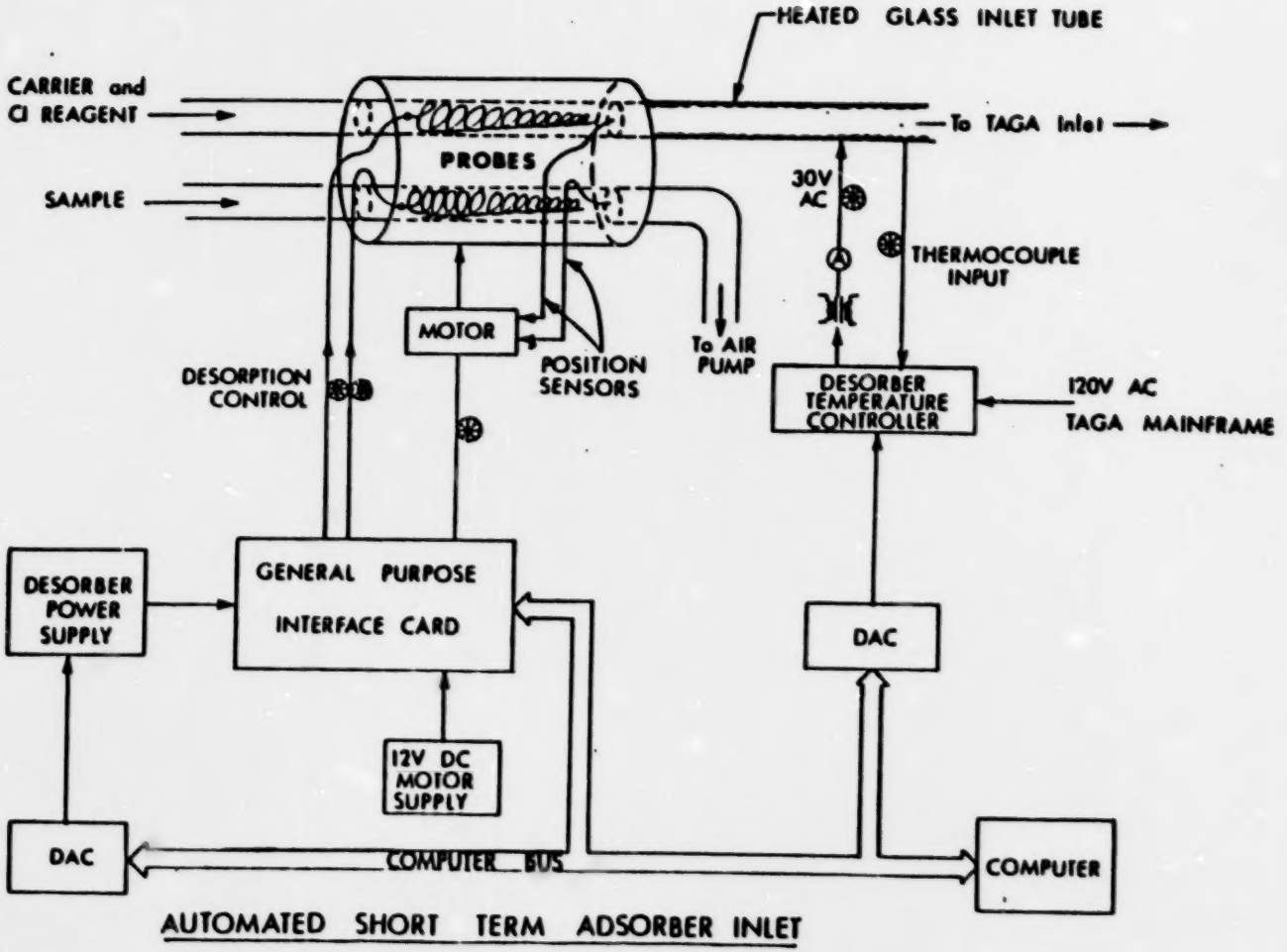


Figure A2: Schematic of the ASTA used in conjunction with the TAGA PCB Monitoring technique.

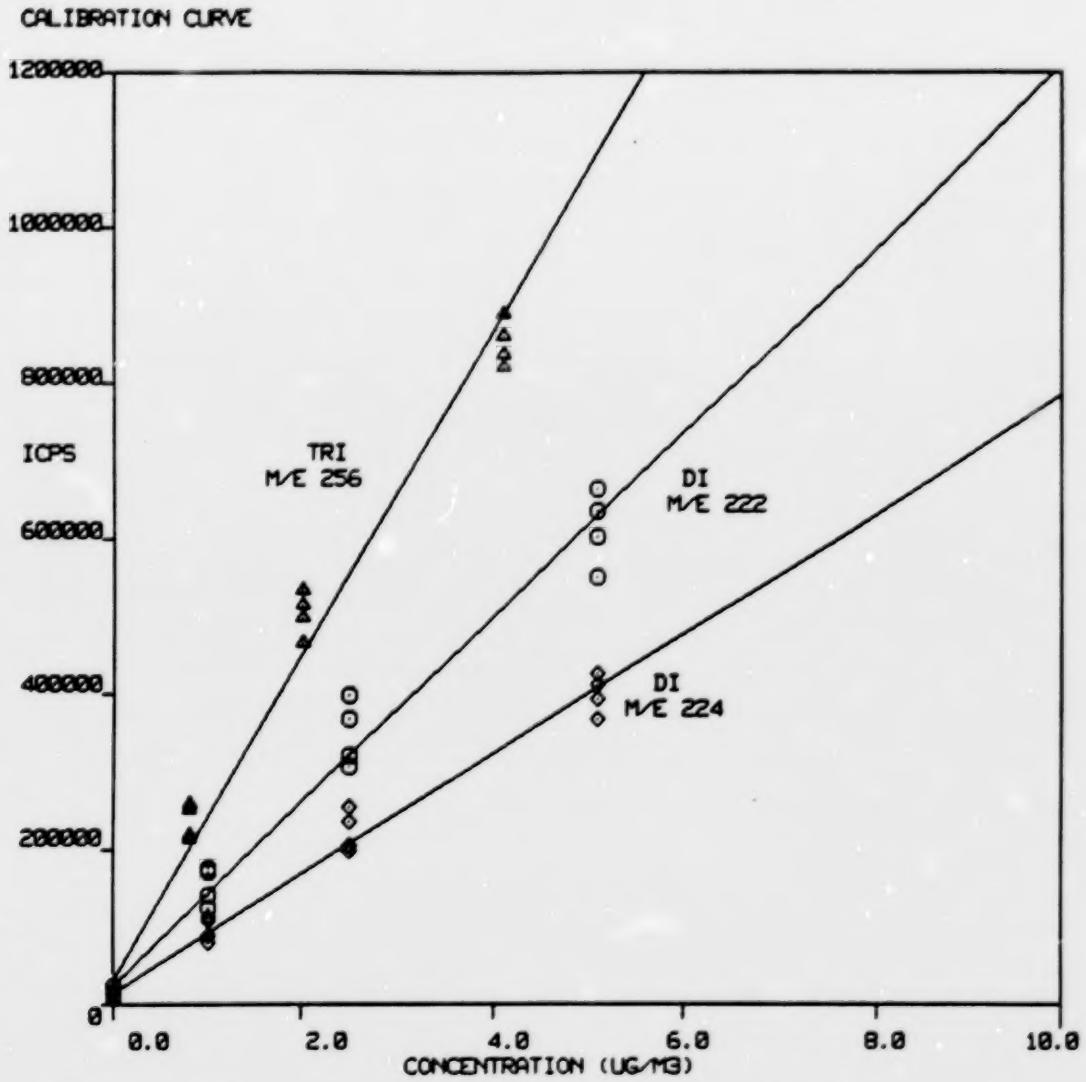
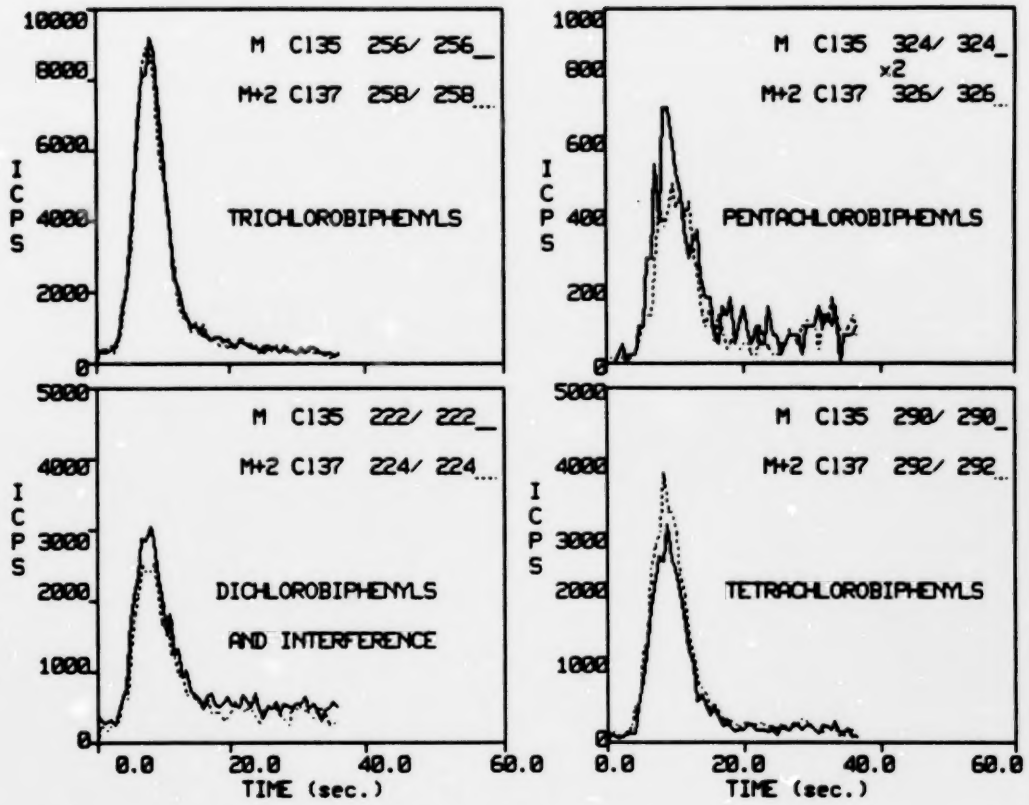


FIGURE A3: EXAMPLE OF CALIBRATION CURVE FOR DI AND TRICHLOROBIPHENYLS

TAGA/ASTA MONITORING TECHNIQUE



MP/MD	MAX.INT	TIM.MAX	INT.IONS	NET	CONC	RATIO TO MP/MD	THEOR.
222/ 222	3053.	8.40	17143.	14691.	0.39i	1.283 224/ 224	1.540
224/ 224	2520.	9.12	13994.	11452.	0.47	0.780 222/ 222	0.650
256/ 256	9213.	8.56	46335.	43368.	0.60	1.056 258/ 258	1.030
258/ 258	8906.	8.64	43545.	41069.	0.62	0.947 256/ 256	0.975
290/ 290	3067.	9.36	14284.	12730.	0.23	0.818 292/ 292	0.769
292/ 292	3800.	8.80	17271.	15562.	0.23	1.222 290/ 290	1.300
324/ 324	360.	9.52	1707.	1303.	0.10	0.620 326/ 326	0.615
326/ 326	507.	10.24	2662.	2099.	0.11	1.612 324/ 324	1.626
					1.3i		

FIGURE A4: Example of TAGA data print-out, PCB analysis. Concentrations are in units of ug/m3. Note the ratio for isotope (222/224) dichlorobiphenyl is mismatched. Total PCB level is computed to be 1.3i ug/m3, where i denotes a contribution by interference at masses 222 and/or 224.